

*On the Emulsifying Action of Soap.—A Contribution to the
Theory of Detergent Action.*

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Although the two closely allied subjects of emulsification and detergent action are of great importance in many branches of technology, they seem to have been very little studied from a scientific point of view. Many technical chemists seem even now to hold the primitive and erroneous view that the detergent action of a soap solution is due to the saponification of grease by the alkali set free by hydrolysis. In the first edition (1893) of Thorpe's 'Dictionary of Applied Chemistry' it is stated that "the value of soap as a detergent is largely due to the fact that contact with water breaks up a neutral soap. . . ." In the new edition (1913) no reference is made to any theory of detergent action. In neither edition is there an article on "Emulsions" or "Emulsification."

It is evident that the theory of these processes is in an unsatisfactory state, as regards both its actual development and its dissemination among those to whom it is of importance. The present paper is the beginning of an attempt at a systematic scientific study of the subject. The first section deals with some theoretical points relating to the process of emulsification, which are in part an amplification of views expressed by one of us in previous papers,* and which are of importance in connection with the subsequent parts of the present paper. The second part deals with some experimental work which we have conducted during the last six months. The results of this work solve a fundamental problem in the theory of detergent action. In the third part is outlined a new theory as to the function of alkali in soap solutions.

§ 1. *General Considerations Relating to the Process of Emulsification.*

It is well known that an emulsion of oil in pure water has, unless very dilute, only a brief existence. Stable concentrated emulsions may be obtained by adding to the water an "emulsifying agent." Such agents may act in two ways: (1) they may prevent the coalescence of the oil droplets, (2) they may facilitate the process of subdivision of the oil. Some agents produce both the above effects, others only the first.

* S. A. Shorter, 'Phil. Mag.,' April, 1909, and April, 1914.

Various theories have been put forward to explain the action of emulsifying agents—such theories being based on considerations of surface tension. Emulsification is not, however, a pure surface tension effect. Many emulsions may be centrifuged till the droplets are tightly packed together, without coalescence occurring. If surface tension effects alone were operative, such treatment would inevitably lead to coalescence.* The true explanation of the effect seems to have been first put forward by Pickering,† who ascribes the effect to the quasi-solidity of the surface layer surrounding each droplet.

In order to understand the process of emulsification one must gain clear ideas as to the mode of formation of such layers. In his famous work ‘On the Equilibrium of Heterogeneous Substances,’ Gibbs‡ proves by means of thermodynamical reasoning that if the further addition of a solute to a solution lowers (raises) the surface tension, the solute will be more (less) concentrated in the surface layers than in the body of the solution. This deduction has been verified qualitatively by several investigators. An effort was made some years ago by Lewis§ to verify the theory quantitatively, but it was found, in the case of many solutions of a colloidal or “semi-colloidal” nature, that the measured values of the “surface excess” were much greater than the values given by Gibbs’s theory. The most satisfactory explanation of this discrepancy is that the process of formation of the surface layer is not the simple reversible effect to which Gibbs’s theory applies. This view is supported by the results of some experiments made by one of us on the surface layers of solutions of saponin, peptone, and albumin.|| It was shown that these substances form surface layers which for small shearing strains are almost perfectly elastic. A method was devised for measuring this elasticity, and thus studying the process of formation of the surface layer. It was found that the process goes on for several weeks without any sign of equilibrium. The substance forming the elastic surface layer separates from the body of the solution at a rate practically independent of the thickness of the layer already formed. The process is thus thermodynamically irreversible, and outside the scope of Gibbs’s theory.

In the case of many other substances, the surface layers do not possess this elasticity, so that their formation cannot be studied in this way. It

* It has been shown by one of us (see S. A. Shorter, ‘Journal of the Society of Dyers and Colourists,’ March, 1915) that an emulsion of carbon tetrachloride in a solution of albumin yields, after repeated centrifuging and replacing of the solution by water, a practically solid mass at the bottom of the tube.

† ‘Chem. Soc. Journ.,’ vol. 91, p. 2001 (1907).

‡ ‘Scientific Papers,’ vol. 1, p. 219.

§ ‘Phil. Mag.,’ April, 1908, and April, 1909.

|| S. A. Shorter, ‘Phil. Mag.,’ February, 1906, and April, 1909.

has been shown, however, by Milner* that the surface tension of a solution of sodium oleate diminishes for a lengthy period after the formation of the surface, and that solid matter can often be detected in a film of the solution.

Solutions exhibiting this irreversible adsorption seem in general to be colloidal, or, at least, "semi-colloidal." The slowness of diffusion of the colloidal particles will evidently cause the process of formation of the adsorption layer to be very slow in the case of a stationary surface. When, however, oil is shaken up with an emulsifying solution, there is a constant renewal of the portions of solution adjacent to the surface layers, so that the process of adsorption is greatly accelerated. On the other hand, it is not generally possible to obtain an emulsion by shaking up a little solution with a relatively large amount of oil. The probable explanation of this is that the motion of the drops of solution through the oil does not renew the portions of solution adjacent to the surface, so that an efficient adsorption layer cannot be formed. Thus it would seem to be a necessary condition for the ready emulsification of one liquid in another, that the emulsifying agent should be in the outer phase. It is possible to emulsify water in certain oils, but these oils are complicated substances, which probably contain some emulsifying agent.

The most striking example of emulsification is that of an animal or vegetable oil (or a mineral oil to which a little fatty acid has been added) by means of a dilute alkaline solution. This case differs very much from cases of emulsification by colloidal agents. This difference is well illustrated by the following experiments: If a little olive oil is poured gently on the surface of a dilute solution of caustic soda, and if the interface is disturbed slightly by means of a glass rod, the oil is projected into the solution in the form of long cylinders, which lengthen till they become extremely thin, and break up into small drops. The process is started with very little agitation—in fact, it is almost spontaneous. If, now, the experiment is repeated with a solution of soap in place of the alkali, it is found the effects produced are similar to those which occur with olive oil and water. A mass of oil is projected into the solution, a "neck" is formed, and the oil is detached in the form of a large drop. This, of course, is an illustration of the instability of long cylinders.

The stability of the long cylinders in the first experiment is evidently due to some modification of the properties of the surface layers. A similar modification is seen if olive oil is shaken up with a solution of alkali too dilute to produce emulsification. The oil is split up into drops, which generally assume quite irregular shapes. There is a complete absence of the

* 'Phil. Mag.,' January, 1907.

clear-cut geometrical shapes and general "cleanliness" of action characteristic of ordinary surface tension phenomena.

It has been shown by Donnan* that the addition of alkali to water has an enormous lowering effect on the surface tension against olive oil†, or a hydrocarbon oil to which a little fatty acid has been added, but has very little effect on the tension against an ordinary hydrocarbon oil or olive oil from which the free fatty acid has been removed. Similarly, an alkaline solution can only emulsify an oil containing free fatty acid. Both effects are evidently due to the formation of soap in the surface layers by the interaction of the alkali and the fatty acid. This soap layer, by reason of its imperfect fluidity, gives rise to the abnormal effects described above.‡

A surface layer of soap may, of course, be formed by adsorption from an actual soap solution. Emulsification by a soap solution is, however, of a much less spontaneous nature than emulsification by alkali. The oil does, indeed, split up much more easily than in the case of pure water, but more shaking is required than in the case of a solution of alkali. As we have seen from the second of the experiments described above, a disturbance of the interface separating olive oil from a soap solution gives rise to effects differing little from the normal surface tension effect. The difference between the alkali and the soap in this respect is readily explained if we consider the question of the rate of formation of the soap layer in the two cases. We have seen that adsorption from colloidal solutions is a very slow process owing to the slowness of diffusion of the colloidal particles. Hence in the case of a soap solution, a rapid extension of the interface thins the soap layer till the interface becomes practically "normal," and exhibits the normal surface tension effect of the instability of long cylinders. In the case of the alkaline solution the alkali is in true solution—as is also the oleic acid in the oil—so that both diffuse rapidly into the interface.§ Hence in the case of a rapid

* 'Zeit. Physikal. Chem.,' vol. 31, p. 42 (1899).

† We ought, of course, to be quite accurate in our phraseology, to speak of the "tension of the interface between water (or a solution) and oil." The above mode of description of the tension is a very convenient one, and receives some degree of justification from the fact that we are concerned mainly with the processes operative in the aqueous phase.

‡ According to Donnan (*loc. cit.*) two emulsion droplets are prevented from coalescing when they collide, by the formation, where they touch, of a layer containing a double amount of adsorbed substance, and having, therefore, a lower tension than the other portions of the surfaces of the droplets. The considerations adduced at the beginning of the present paper show that this theory is quite untenable. It may be pointed out that the important part played by the quasi-solidity of the surface layers of soap solutions was fully recognised by Gibbs in the year 1878 (see 'Scientific Papers,' vol. 1, p. 312).

§ The alkali is, moreover, ionised in solution.

extension of the interface, the formation of the soap layer keeps pace with the extension, and modifies the mechanical properties of the surface so that the formation of long cylinders is possible.

The fact that soap solutions appear, from a superficial examination, to behave towards an oil containing free fatty acid more like other colloidal solutions than like a solution of alkali, does not entirely exclude the possibility that hydrolysis alkali may have some effect. We will consider this question in the next section.

§ 2. *The Surface Activity of the Hydrolysis Alkali.*

The theory that the detergent action of soap is mainly due to saponification effected by the alkali set free by hydrolysis is conclusively disproved by the experiments of Donnan, which show that the lowering of the interfacial tension produced by alkali, and its emulsifying power, depend upon the presence of free fatty acid in the oil. It has been argued by Hillyer* that hydrolysis alkali cannot effect any saponification of glycerides in an oil, since, if it were capable of doing this, it would be equally capable of attacking the acid products of hydrolysis. A similar argument might, of course, be applied to the case of the neutralisation, by hydrolysis alkali, of the free fatty acid in an oil. Hillyer's argument is, however, unsound. The hydrolysis alkali does attack the acid products—but the effect of this is counterbalanced by the decomposition of the soap. This is a fundamental idea in the theory of chemical equilibrium.

The present state of our knowledge is, therefore, that we know from experimental evidence that saponification plays no part in emulsification by alkali, and that alkali is capable of a surface reaction with free fatty acid in an oil. We may safely conclude that with regard to saponification, hydrolysis alkali is no more efficient than ordinary alkali. We are therefore left with the unsolved fundamental problem of determining whether or not hydrolysis alkali is capable of a surface reaction with free fatty acid. With the object of solving this problem we have made a series of experiments. The principle underlying these experiments is very simple. The addition of alkali to water has very little effect on the surface tension against a hydrocarbon oil, but has an enormous effect if a little fatty acid be added to the oil. The solution of the problem, therefore, lies in determining how the surface tension of a soap solution against a mineral oil is affected by the addition of fatty acid to the latter. The general plan of the experiments was as follows. A stock solution was made up containing known amounts of oleic acid and caustic potash.

* 'Journ. Amer. Chem. Soc.,' vol. 25, p. 511 (1903).

Solutions were made up by diluting this stock, and stalagmometric observations were made on them, using in the stalagmometer, first, pure benzene, and then benzene containing a little oleic acid (2.034 grm. per litre). The process was repeated with several different stock solutions, beginning with an excess of alkali, and ending with an excess of acid.

The stalagmometer was constructed from a 5-c.c. pipette. The lower end was bent through 180° , so that the instrument could be used for an oil lighter than water. The fundamental difficulty in the use of the stalagmometer is the variability of the effective size of the hole at which the drops are formed. This variability is due to changes in the extent of the surfaces of glass wetted respectively by the benzene and by the solution. The usual method of overcoming this difficulty is to make the lower end of the instrument of thin-walled tubing, so that the maximum and minimum values of the effective orifice are nearly equal. We, however, went to the other extreme, and ground the lower end of the pipette flat. This made the orifice practically a hole in a flat disc, so that the drops formed either correctly on the actual hole, or obviously incorrectly over the whole plane area (whose diameter was about two and a half times that of the hole). Several pipettes were ground down before one was found with a sufficiently nearly circular orifice. As the volume of the bulb of the pipette was too large for rapid working, a small bulb was blown on the upper part of the stem. The volume between the marks made on either side of it was about 1.2 c.c. This size of bulb gave a suitable compromise between rapidity and accuracy. Flat glass cells were used for holding the solutions. These had the advantages of requiring a small amount of solution, and of allowing the process of drop formation to be readily observed in the case of turbid solutions. In order to render the rate of issue of the benzene sufficiently slow, a piece of glass tubing, drawn out at one end to a long fine capillary, was attached by means of a short piece of rubber tubing to the top end of the stalagmometer. The flow of the benzene was thus regulated by air friction in the capillary. If, as occasionally happened, the capillary were broken, it was quite easy to adjust another tube to give the same rate of flow.*

The method of taking a reading was as follows: The short piece of rubber tube was attached to the top end of the stalagmometer and closed with a clip. The rubber tube was then attached to a glass tube connected with a

* We find that this convenient device of using an air-friction capillary instead of the usual liquid friction capillary in the body of the stalagmometer has also been adopted by Cooper and Nuttall ('*Journal of Agricultural Science*,' vol. 7, Part II, p. 219 (September, 1915)).

filter pump, and the lower end of the stalagmometer dipped into a small vessel filled with benzene. By cautiously opening the clip, the benzene was drawn to a convenient distance above the upper mark. The instrument was then clamped in position above the cell holding the solution, the air tube was fixed in position, the clip removed, and the stalagmometer lowered into the solution. The removal of the clip (and consequent increase in the internal volume of the rubber tube) caused at first the benzene to retreat from the stalagmometer orifice, leaving an air space. If the stalagmometer were lowered into the solution too soon, some of the solution entered it, and sometimes was not driven out by the benzene, but collected in drops below the orifice, giving trouble by coming out during the dropping. In any case, the presence of the solution in the stalagmometer is objectionable. A too early introduction of the instrument into the solution was therefore to be avoided. On the other hand, if one waited till the benzene actually issued from the orifice, the drops were apt to form in the wrong manner (over the plane area). This could generally be remedied by jerking to and fro either the stalagmometer or the vessel containing the solution. Experience showed that the risk of wrong drop formation was the less of the two evils, and the stalagmometer was always immersed as soon as possible after the benzene had reached the orifice. On some days the instrument behaved very badly, the drops persistently forming in the wrong manner. In such cases a thorough cleansing of the instrument with hot soap solution, and subsequent rinsing and drying, always effected a cure. At the conclusion of a reading the stalagmometer was raised out of the solution, the benzene was allowed to flow for a few seconds more, the clip was closed, the air tube removed, and the lower end of the stalagmometer wiped with a clean cloth, after which it was ready for refilling.

In making up the stock solutions 200 c.c. of N/10 caustic potash solution were taken, diluted and heated to the boiling point. The oleic acid was then run in slowly, and the mixture heated again, being well stirred all the time. The volume of the solution was finally made up to 250 c.c. Ordinary commercial oleic acid was used. A simple calculation shows that the amount of oleic acid equivalent to the alkali in the stock is 5.646 gm. It would, however, have been obviously unsafe to base any calculations relating to the composition of the stock solutions on this number. In order to investigate the point further, a solution of caustic potash in absolute alcohol was made up, and its strength determined by titration against a standard hydrochloric acid solution. The oleic acid was then titrated against the alcoholic potash solution, phenolphthalein being used as indicator. The details of the determination are as follows. The concentration of the potash solution was

found to be 1.594 N. A volume 60 c.c. of the potash solution was taken, a little phenolphthalein was added, and rather less than the equivalent amount of oleic acid was run in. The solution was then boiled for about 10 minutes. More oleic acid was then added drop by drop, the solution being boiled for a few minutes after the addition of each drop. In spite of the fact that the final solution was a dark-brown colour, there was no difficulty in determining the end-point satisfactorily. The volume of oleic acid required to neutralise the alkali was 30.15 c.c. This amount is equivalent to $60 \times 1.594/1000$ gramme-molecule of alkali. Each stock solution contains 0.02 gramme-molecule of alkali. The volume of oleic acid equivalent to this is therefore 6.305 c.c. The density of the oleic acid was found to be 0.895 gm./c.c., so that this volume weighs 5.643 gm.—a value which does not differ appreciably from that calculated on the assumption that the oleic acid is pure. This agreement does not, however, indicate a correspondingly high degree of purity of the acid used, but merely that the impurities are mainly fatty acids or glycerides whose equivalent weights do not differ appreciably from that of oleic acid. The above result was verified by other determinations.

The results of the series of experiments are shown in Table I. The numbers at the head of the pairs of columns of drop numbers are the values of the ratio of the number of equivalents of acid to that of alkali (*i.e.* the number of cubic centimetres of acid used in making up the stock solution divided by 6.305). The concentrations of the total alkali (in gramme-molecules per litre) are given in the first column. In the case of solutions containing excess of acid, the concentration of the soap is equal to that of the total alkali. In the case of solutions containing excess of alkali, the concentration of the soap is equal to the product of that of the total alkali and the ratio of acid to alkali, while the difference between these two concentrations is equal to the concentration of the excess alkali. It need hardly be remarked that these values do not give the actual composition of the solutions, but merely indicate how the solutions could be made up from pure solid potassium oleate and alkali or oleic acid. The concentration of the excess alkali will always be less than that of the free alkali, the difference being that of the hydrolysis alkali.

Solutions containing a large amount of excess alkali have a much larger drop number against the acidified benzene than against pure benzene. This, of course, is due to the interaction in the surface layers of the free alkali and the oleic acid in the benzene. From Table I we see that the acidified benzene drop number exceeds the pure benzene drop number not merely in the case of a solution of a neutral soap, but also when the oleic acid is in considerable excess. This would seem to indicate that hydrolysis alkali,

Table I.—Drop Numbers of Solutions.

(a) Against Pure Benzene.

(b) Against Acidified Benzene.

Concentration of total alkali.	Ratio of acid to alkali.											
	0·951		0·999		1·030		1·109		1·189		1·426	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0	15½	16½	15	16½	15½	16½	15¼	16½	14½	16½	15¼	17
0·0016	24½	31	23½	32½	26	30	—	30½	23½	28	—	—
0·0032	33½	44½	35½	48½	36½	44½	31½	41½	29½	37	28½	31½
0·0064	47	70	48½	66½	47½	64	42	55	40½	51½	36	42
0·0096	53½	79½	54½	76½	53½	75½	49¼	63	44	54	41½	51½
0·0136	62	89	59	84	57½	81½	52½	69	48	61½	45	57
0·0208	67½	99	64	92	61	88	56	74½	51½	68	48½	61½
0·0320	72	107½	68	99	64½	94	58	77	54	71	52	65½
0·0560	73	122	70½	108	66	100	59	74	54½	70½	53	67½
0·0800	—	138	71½	113½	66	104	59	77	—	70	52½	67½

like ordinary alkali, is capable of interaction with the oleic acid in the benzene. This point must, however, be examined more closely. The addition of oleic acid to the benzene increases the drop number against pure water, so that even if the hydrolysis alkali had no effect, we should still expect the acidified benzene drop number to be greater than the pure benzene drop number. The averages of a large number of determinations of the drop numbers in the case of pure water, gave for the ratio of the two the value 1·09. Now in the case of the results shown in the fourth and fifth columns of Table I (which relate to a practically neutral soap) the ratio of the two drop numbers is much greater than this. Thus in the case of the 0·0096 N solution the ratio is 1·40. We may therefore safely conclude that hydrolysis alkali is capable of forming with the fatty acid in an oil a surface layer of soap. It will be seen that this effect persists even when the oleic acid is in large excess. This is not surprising when we consider that the acid products of hydrolysis have only a very small true solubility, and that the suppression of hydrolysis caused by the excess oleic acid will therefore be small.

In the absence of any definitely established principle of additivity, it is not possible to compare quantitatively in any thoroughly satisfactory manner the "surface activity" of the soap and the alkali. We will, however, adopt the following crude method of comparison. Let N and N_a be the drop numbers of a soap solution against pure and acidified benzene respectively. Let n and n_a be the corresponding values in the case of pure water. Owing to the action of the alkali in the solution on the oleic acid in the benzene we have $N_a > N$. If there were no such action we should not have $N_a = N$,

since $n_a > n$. Let us assume that in the absence of any action of the alkali the drop number of the solution against the acidified benzene would be Nn_a/n . We may now regard the effect of the alkali to be a change of the drop number from Nn_a/n to N_a . We will call the ratio $N_a n / Nn_a$ the "surface activity ratio" of the alkali. The actual magnitude of the "surface activity" will, of course, be measured by the logarithm of this ratio, just as the magnitude of a musical interval is measured by the logarithm of the ratio of the frequencies of the notes. The values of the "surface activity ratio" for the different solutions are shown in Table II. The values are tabulated for a series of equidistant values of the concentration of the potassium oleate, the necessary values of the drop number being obtained from the experimental results by graphical interpolation.

Table II.—Values of the "Surface Activity Ratio" of the Free Alkali.

Concentration of potassium oleate.	Ratio of acid to alkali.					
	0·951	0·999	1·030	1·109	1·189	1·426
0·01	1·31	1·28	1·30	1·17	1·16	1·14
0·02	1·37	1·32	1·31	1·21	1·19	1·15
0·03	1·36	1·32	1·33	1·20	1·19	1·14
0·04	1·43	1·35	1·34	1·19	1·20	1·16
0·05	1·50	1·37	1·37	1·18	1·20	1·17
0·06	1·57	1·39	1·38	1·18	1·18	1·16
0·07	1·65	1·43	1·39	1·19	1·18	1·16
0·08	1·74	1·45	1·43	1·19	—	—

It will be seen that this ratio increases much more slowly with the concentration in the case of solutions of a neutral soap than in the case of solutions containing excess of alkali. This is due, of course, to the fact that the concentration of the hydrolysis alkali does not increase proportionately to the concentration of the soap, as does that of the excess alkali.

We have assumed that the effect of the undecomposed soap is to change the acidified benzene drop number from n_a to Nn_a/n , *i.e.* in the ratio N/n . The ratio of the "surface activity" of the alkali to that of the soap is therefore equal to

$$\frac{\log (N_a n / N n_a)}{\log (N / n)}.$$

The values of this ratio are given in Table III.

It will be seen that in the case of solutions of a neutral soap the "surface activity" of the hydrolysis alkali is only about one-fifth of that of the undecomposed soap. In drawing any conclusion as to the relative effects of

Table III.—Ratio of the “Surface Activity” of the Free Alkali to that of the Undecomposed Potassium Oleate.

Concentration of potassium oleate.	Ratio of acid to alkali.					
	0·951	0·999	1·030	1·109	1·189	1·426
0·01	0·21	0·19	0·21	0·13	0·14	0·13
0·02	0·22	0·20	0·19	0·15	0·15	0·12
0·03	0·20	0·19	0·20	0·14	0·14	0·11
0·04	0·23	0·20	0·20	0·13	0·15	0·12
0·05	0·26	0·21	0·22	0·12	0·15	0·13
0·06	0·29	0·22	0·22	0·12	0·13	0·12
0·07	0·32	0·23	0·23	0·13	0·13	0·12
0·08	0·35	0·24	0·25	0·13	—	—

soap and hydrolysis alkali in ordinary cases of detergent action, we are faced with the question as to whether the acidified benzene used in our experiments can be regarded as a fair sample, as regards fatty acid content, of the greasy matter commonly occurring on dirty materials. The value of the ratio of the two “surface activities” will, of course, depend on the concentration of the oleic acid in the benzene. When the molecular concentration of the oleic acid becomes much greater than that of the hydrolysis alkali this dependence will probably be slight. The concentration of the oleic acid in the acidified benzene used was about 0·007 N, a value much larger than that of the hydrolysis alkali in any of the solutions used. We may, therefore, safely conclude that in cases of detergent action with solutions of neutral soaps, the emulsifying action is due mainly to the undecomposed soap. Whether we can make this statement more extreme, and say that in all cases the undecomposed soap plays a very much more important part than the hydrolysis alkali, can only be decided by experiments on oily substances which occur on dirty materials.*

The question naturally arises as to whether it is possible to draw any conclusions as to the degree of hydrolysis of the potassium oleate. The first step towards this is obviously to investigate the “surface activity” of alkali

* It may be pointed out that emulsification is only one of three functions of a detergent, which are—(1) the wetting of a greasy surface, (2) emulsification, (3) the stabilising of the very fine suspension (and emulsion) which results from the initial emulsification. The first two of these depend upon surface tension relationships, but the third depends upon the colloidal nature of the detergent solution. A dilute solution of alkali is an excellent emulsifier of a gross mass of oil containing free fatty acid, but is of no use as a detergent, since, like solutions of other electrolytes, it tends to coagulate a fine suspension (see Jackson, Cantor Lectures “On Bleaching Agents and Detergents used in Laundry Work,” Lecture III).

in water. Solutions of caustic potash were therefore made up, and the drop numbers measured against pure and acidified benzene. Commercial caustic potash, which would contain a certain amount of potassium carbonate, was used. The solutions were made up from two stock solutions, whose concentrations were determined by titration with a standard sulphuric acid solution. The results of the stalagmometric observations are given in Table IV.

Table IV.

Concentration of caustic potash.	Drop number.	
	Pure benzene.	Acidified benzene.
0	$15\frac{3}{4} : 15\frac{1}{2}$	$17\frac{1}{2}$
0·000444	$16\frac{1}{2} : 16\frac{1}{4}$	$22\frac{1}{4}$
0·000889	—	$34\frac{3}{4}$
0·001185	—	45
0·001481	—	63 : 69
0·001777	—	87
0·00200	—	115
0·00222	—	180
0·00889	$16\frac{3}{4}$	—
0·0889	17	—
0·917	$22\frac{1}{4}$	—

It will be seen that the caustic potash has practically no effect on the surface tension against pure benzene, so that the lowering effect in the case of the acidified benzene may be ascribed entirely to the interaction between the alkali and the oleic acid. In order to draw any conclusions as to the degree of hydrolysis of the potassium oleate, it is necessary to make some assumption as to the additivity of the "surface activities" of the oleate and the alkali. The simplest assumption we can make is that the free alkali (excess and hydrolysis) alters the drop number which the soap solution would have if the alkali had no effect (*i.e.* Nn_a/n), in the same ratio as the pure water drop number is altered by the addition of the same amount of alkali. Now we can experiment not merely with "neutral" solutions, in which all the free alkali is hydrolysis alkali, but also with "alkaline" solutions, in which we know the concentration of the excess alkali (and therefore an inferior limit to the concentration of the free alkali). We can, therefore, proceed to test the validity of the above assumption by comparing the "surface activity ratio" of the free alkali in an "alkaline" soap solution (*i.e.* $N_a n / N n_a$) with the ratio of the drop number of a solution of caustic potash of concentration equal to that of the excess alkali, to the drop number of pure water (a ratio which may be called the "surface activity

ratio" of the excess alkali in pure water). The results of such a comparison in the case of two sets of solutions are shown in Table V. The first half of the Table deals with the results given in the second and third columns of Table I. The second half relates to solutions made from a much more strongly alkaline stock, in which the ratio of acid to alkali was 0.713. The necessary values of the drop numbers of the solution of caustic potash were obtained from the experimental results given in Table IV by graphical interpolation.

If the assumption regarding the additivity of the effects were true, we should find that the "surface activity" of the free alkali in the soap solution was always greater than that of the excess alkali in pure water, the difference being the "surface activity" of the hydrolysis alkali. It will be seen, however, that the numbers in the third column of Table V are in most cases

Table V.

Concentration of		"Surface activity ratio" of	
Potassium oleate.	Excess alkali.	Free alkali in solution of potassium oleate.	Excess alkali in water.
0.0015	0.0001	1.15	1.09
0.0030	0.0002	1.53	1.12
0.0061	0.0003	1.37	1.24
0.0091	0.0005	1.36	1.35
0.0129	0.0007	1.32	1.65
0.0198	0.0010	1.35	2.29
0.0304	0.0016	1.37	4.00
0.0533	0.0027	1.53	Very large.
0.0761	0.0039	1.74	"
0.0011	0.0005	1.39	1.35
0.0017	0.0007	1.60	1.65
0.0023	0.0009	1.71	2.06
0.0029	0.0011	1.94	2.53
0.0034	0.0014	2.01	3.24
0.0040	0.0016	2.23	4.24
0.0046	0.0018	2.60	5.53

less than the corresponding numbers in the fourth column. The "surface activity" of alkali in a soap solution is therefore less than that of the same concentration of alkali in water, so that we cannot use the above principle of additivity to calculate the concentration of the hydrolysis alkali. In the case of the strongest two solutions dealt with in Table V, it will be seen by reference to Tables I and IV that the acidified benzene drop numbers are actually less than those of solutions of caustic potash of concentrations equal respectively to the concentrations of the excess alkali. In the case of the

more dilute solutions the numbers in the third column are greater than those in the fourth column. This is due to the fact that owing to hydrolysis the concentration of the free alkali is much greater than that of the excess alkali.

§ 3. *The Effect of Alkali on the "Surface Activity" of the Potassium Oleate.*

An examination of the pure benzene drop numbers given in Table I reveals the interesting fact that the addition of alkali to a soap solution increases the drop number against pure benzene. Now there can be no specific action such as occurs with acidified benzene, so that the alkali must in some way increase the "surface activity" of the soap. The most obvious explanation of the effect is that the alkali increases the amount of undecomposed soap in the solution by suppressing the hydrolysis.

With the object of investigating this effect we made a series of observations of the pure benzene drop numbers of solutions containing excess of alkali. The results of these observations, together with some of those previously obtained, are given in Table VI.

Table VI.—Drop Numbers against Pure Benzene.

Concentration of total alkali.	Ratio of acid to alkali.									
	0·0317	0·0792	0·158	0·317	0·793	0·872	0·999	1·030	1·236	1·426
0·0032	22	26½	33½	38½	36	34½	35½	36¼	30½	28½
0·0064	33	49	63	75	59	49½	48½	47½	40	36
0·0096	47	71	86	97	75	58	54½	53½	44½	41½
0·0136	63	90	97	111	88	69	59	57½	48½	45
0·0208	86	107	106	124	101	81	64	61	52½	48½
0·0320	103	118	126	133	110	95	68	64½	55	52
0·0560	124	130	133	139	118	109	70½	66	56½	53
0·0800	138	137	139	148	127	126	71½	66	56	52½

It is easy to see that the effect is much too great to be explained by the suppression of hydrolysis. Thus the solution in which the ratio of acid to alkali is 0·0317, and the concentration of total alkali 0·0208 N, contains only 0·00066 gramme-molecule of potassium oleate per litre, and yet has a drop number larger than that of the 0·08 N solution containing no excess alkali.

The above Table does not show directly the effect of adding increasing amounts of alkali to a soap solution of constant concentration, though it is quite easy to compile, by graphical interpolation, Tables showing this effect for various constant concentrations of soap. The addition of alkali to

a solution of neutral soap causes at first a rapid increase in the drop number, but the effect diminishes as the amount of excess alkali increases. The effect of a given addition of alkali is the greater the smaller the constant concentration of the soap. We have verified these general features of the effect by direct addition of alkali to various constant concentrations of other soaps. We also find that caustic soda gives, with a potassium soap, approximately the same effect as caustic potash.

Starting from a drop number in the eighth column of Table VI and moving along a row from right to left, corresponds to gradually replacing the potassium oleate in a "neutral" solution by an equivalent amount of alkali. This must ultimately cause the drop number to approach a value differing very little from the pure water value ($15\frac{1}{2}$). In the case of the more concentrated solutions the drop numbers do not show any marked decrease till the ratio of acid to alkali has become extremely small.

In order to formulate any theory of this effect, we must consider the nature of aqueous soap solutions. With respect to water as solvent, soaps may be classed as "semi-colloids." A "semi-colloid" exists in solution in the form of particles of various sizes, the smallest approximating to simple molecules, the largest being large enough to produce the Tyndall effect. Now, colloids are in general more "surface active" than substances in true solution. In fact, the phenomenon of irreversible adsorption (of which the adsorption of soap is an example) seems to be the exclusive property of colloids. We therefore suggest, as an explanation of the effect, the theory that the alkali exerts a coagulative effect on the soap, *i.e.* increases the average size of the particles in the solution, and thus increases the "surface activity" of the soap. We may describe this effect by saying that the alkali increases the colloidal nature of the soap.

Further investigation is necessary before more can be said as to the precise mode of action of the alkali. One suggestion that immediately presents itself is that the alkali acts as an electrolyte—the instability that ultimately results in the "salting out" of the soap being anticipated in the surface layers. If the effect is merely this species of "incipient salting out" of the soap, it should be produced by a salt such as potassium chloride. Experiment shows that both potassium and sodium chlorides increase the "surface activity" of the soap, but the effect is much smaller than that of alkali. Further investigations relating to this effect are at present in progress.

The question of the effect of alkali on soap solutions is, of course, of importance in relation to the theory of detergent action. It is well known that a small amount of alkali increases enormously the detergent power of a

soap solution. According to Jackson,* the effect is due partly to the direct emulsifying action of the alkali, and partly to the suppression of hydrolysis. We have seen, however, that in cases where the former cause cannot operate, the latter is quite inadequate to explain the effect—which must be due to some more profound modification of the properties of the solution. The question is complicated by the fact that in most ordinary cases of detergent action the greasy matter contains free fatty acid. It is a common practice, however, to use an extra amount of alkali in scouring materials stained with mineral oils. This highly interesting fact proves conclusively that the effect of the alkali on the “surface activity” of the soap is a factor comparable in importance with, if not more important than, the independent effect of the alkali.†

§ 4. *Conclusion and Summary.*

The results given in the present paper are sufficient to show that the stalagmometer may be made to yield valuable information regarding these properties of soap solutions which are of importance in relation to detergent action. The present investigation is limited, in that it deals only with the single compound potassium oleate, and in that all the experiments have been carried out at ordinary room temperatures. Besides the obvious extension of the work beyond these limitations, there are two subjects which seem likely to repay further investigation. One is the diminution of the “surface activity” of alkali by the addition of soap; the other is the increase of the “surface activity” of soap by the addition of alkali. It is possible that these two effects are closely connected with each other, so that an investigation of them will throw much light on the processes operative in soap solutions.

The results of the present investigation may be summarised as follows:—

(1) The hydrolysis alkali in a soap solution is capable of assisting in the formation of the soap surface layer, by interacting with the free fatty acid in an oil.

(2) The “surface activity” of the hydrolysis alkali, in the case of oils

* Cantor Lectures, “On Bleaching Agents and Detergents used in Laundry Work,” Lecture II.

† The increased “surface activity” of the soap may increase the detergent power in two ways—(1) by increasing the wetting power of the solution, (2) by increasing its emulsifying power. The difficulty of scouring a material stained with a mineral oil may be due to the low tension (against air) of the oily surface, and consequent difficulty of wetting it. The increased “surface activity” of the soap (*i.e.* the lowering of the tension of the interface between the soap solution and the oil) may operate chiefly by causing the solution to spread more readily over the material.

containing small amounts of free fatty acid, is much smaller than that of the undecomposed soap.

(3) The "surface activity" of free alkali in a soap solution is less than that of the same concentration of alkali in water.

(4) The addition of alkali to a soap solution increases the "surface activity" of the soap.

(5) This effect is much too large to be explained by the suppression of hydrolysis.

(6) It is suggested that the effect is partly due to an increase in the colloidal nature of the "semi-colloidal" soap solution.*

The Consumption of Carbon in the Electric Arc. No. III.—*The Anode Loss.*

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1. In a previous communication to the Royal Society† experiments conducted in the Physical Laboratory of University College, Reading, have been described, from which it appears that the rate of consumption of carbon from the cathode of a very short arc is such that the departure of one atom is accompanied by the transference between the poles of four electronic charges. The loss of weight of the anode is larger than this, on account of subsidiary combustion or evaporation occasioned by the high temperature of the crater.

An experiment has been described in the paper referred to which demonstrates the supreme importance of a hot cathode; the arc could be maintained with a hot cathode alone, but not with a hot anode alone. It was suspected in consequence of this that the anode consumption of carbon was unimportant, and the experiment was repeated in the following manner for the purpose of testing this.

* It may be pointed out that many of the facts relating to the effect of electrolytes on the adsorption of dyestuffs may be explained by the effects produced on the colloidal state of the dye, and on the potential difference between the fibre and the solution. See Harrison, "The Electrical Theory of Dyeing," 'Journal of the Society of Dyers and Colourists,' December, 1911.

† Duffield, 'Roy Soc. Proc.,' p. 122, *supra*.